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SYNTHETIC WODGINITE, TAPIOLITE AND TANTALITE

by

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Mineral Sciences Division Report MS-65-48

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A.C. Turnock*

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ABSTRACT

Solid phases in the systems $MnTa_2O_6$-$FeTa_2O_6$-O and $MnTa_2O_6$-$FeTaO_4$ have been synthesized at various temperatures and partial pressures of oxygen.

In the binary system $MnTa_2O_6$-$FeTa_2O_6$, the two solid phases produced were: (i) orthorhombic $Mn_{1-x}Fe_xTa_2O_6$ (tantalite), and (ii) tetragonal $Fe_{1-y}Mn_yTa_2O_6$ (tapiolite). The maximum amounts of substitution at 1200°C were $x = 0.18$, $y = 0.62$.

The oxidation of these tantalites and tapiolites (the system $MnTa_2O_6$-$FeTa_2O_6$-O) produced solid phases with compositions that are on the join $MnTa_2O_6$-$FeTaO_4$, plus exsolved Ta_2O_5.

In the system $MnTa_2O_6$-$FeTaO_4$, the three solid phases produced were: (i) orthorhombic $MnTa_2O_6$ (tantalite), (ii) monoclinic $Mn^{+2}_{2-2w}Fe^{+3}_{3w}Ta_{4-w}O_{12}$ with $0.08 < w < 0.29$ at 1200°C (wodginite), and (iii) tetragonal $Fe^{+3}_{3-3z}Mn^{+2}_{2z}Ta_{3+z}O_{12}$ with $0 \leq z < 0.57$ at 1200°C, a compound with a rutile-type structure.

It has been shown that in wodginite (i) the iron is trivalent and the manganese divalent, and that (ii) tin is not an essential component.

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INTRODUCTION

Wodginite was discovered by E.H. Nickel in pegmatite from Bernic Lake, Manitoba, and further study led to a definition of this mineral (Nickel, Rowland and McAdam, 1963a). It was found to be chemically and structurally related to columbite-tantalite.

Chemically, both wodginite and columbite-tantalite are complex oxides of Fe, Mn, Ta and Nb, with minor substitutions by Ti and by Sn, with cations: anions = 1:2. Columbite-tantalites have the formula $(Mn, Fe)_4(Nb, Ta)_8O_{24}$ (or $4 \times AB_2O_6$). Nickel et al. found wodginite to be $A_{16}O_{32}$, where A represents chiefly Ta, Mn and Sn. It is demonstrated in the present paper that tin is not an essential element for the formation of wodginite, that it may contain ferric but not ferrous iron, and that it is a solid solution between the AB_2O_6 and ABO_4 types.

The similarity of the crystal structures of wodginite and columbite-tantalite was deduced by Nickel, Rowland and McAdam (1963a), who found the unit cells to be related by: $a_W \Xi 2/3\, b_C$, $b_W \Xi 2a_C$, and $c_W \Xi c_C$ (subscripts W and C for wodginite and columbite-tantalite, respectively). Wodginite is monoclinic ($\beta = 91° 18'$), whereas columbite-tantalite is orthorhombic; this difference involves only a slight distortion without destroying the structural similarity.

The structural similarity of columbite to wolframite was noted by Schröcke (1961), and detailed by Laves, Bayer and Panagos (1963). Broch (1929) originally discussed as the "wolframite-group" some ABO_4 compounds that had similar structures; Laves et al. (1963) and also Roth and Waring

(1964) have expanded and formulated this family relationship. The group contains both orthorhombic and monoclinic members, structurally related by a slight distortion; this behaviour is exemplified by the wolframite series, where the angle β changes from 90° 00' in $FeWO_4$ to 91° 10' in $MnWO_4$ (Sasaki, 1959). The unit cell of columbite may be described as a supercell formed by triple repetition of an orthorhombic wolframite sub-cell along one axis (the a of wolframite in its usual setting with a = 4.78, b = 5.73, c = 4.98), caused by ordering of the cations. The unit cell of wodginite, which must be added to this group, may be described as a super-cell of a monoclinic wolframite sub-cell, with double repetition along the a and b axes.

EXPERIMENTAL PROCEDURE

Crystalline materials were synthesized from reagent-grade chemicals, and were reacted in a quench furnace under controlled conditions of temperature and partial pressure of oxygen. The total pressure was one atmosphere for all experiments. The partial pressure of oxygen was varied by adjusting the composition of the gas or gas mixture that passed through the furnace from bottom to top. Air, oxygen and mixtures of CO_2 and CO were used.

It was found that chemical mixtures, viz., $Fe_2O_3 + MnC_2O_4.2H_2O + Ta_2O_5$, or $FeC_2O_4.2H_2O + MnC_2O_4.2H_2O + Ta_2O_5$, reacted quickly when heated at temperatures higher than 1000°C to produce the more stable complex oxides. At 1200°C the reactions were completed

in two hours.

At the completion of the heating time, the charge was lowered to the cool end of the furnace, where it cooled to room temperature in the stream of gas entering the furnace in about half a minute. No reactions were suspected to take place during this cooling period.

Oxidation and reduction reactions between the synthetic solids and vapour were also investigated. Any changes in the bulk composition, caused by changes in the oxygen content, were determined from weight changes.

The phases formed were identified by powder X-ray diffraction examination.

THE SYSTEM $MnTa_2O_6$ - $FeTa_2O_6$

In order to keep both the manganese and iron in the divalent state, as required in this system, the partial pressure of oxygen (f_{O_2}) in the furnace was controlled at a low value, i.e., the univariant f_{O_2} of the iron wüstite equilibrium, by using mixed gases with $CO:CO_2$ in the appropriate ratios as determined by Darken and Gurry (1945).

The products of synthesis were either one or both of the following phases: (i) orthorhombic $Mn_{1-x}Fe_xTa_2O_6$, here referred to by its mineral name tantalite, and (ii) tetragonal $Fe_{1-y}Mn_yTa_2O_6$, here referred to as tapiolite. Their distribution is shown in Figure 1.

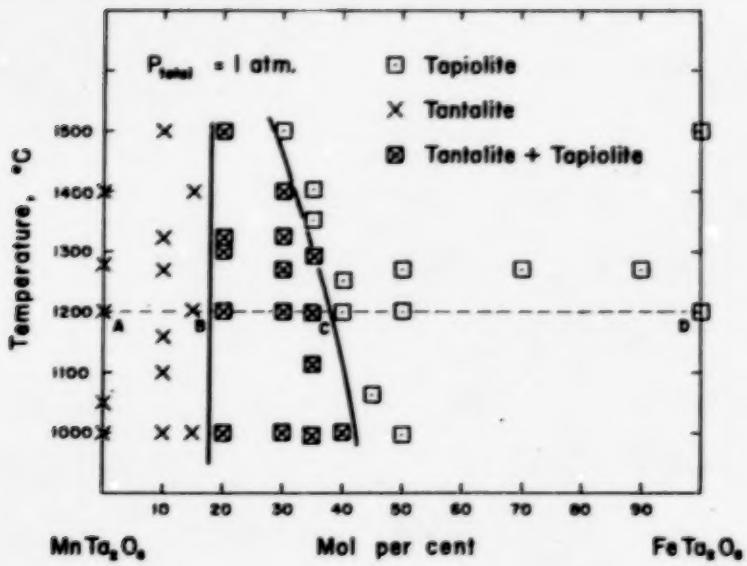

Figure 1. The system $MnTa_2O_6$-$FeTa_2O_6$. The data points present the results of synthesis for various lengths of time, plus reversals of the equilibrium along the tapiolite field boundary.

Tantalite can take up to 18 mol. % $FeTa_2O_6$ into solid solution, and this limit appears to be insensitive to temperature variation. By contrast, the maximum amount of solid solution of $MnTa_2O_6$ in tapiolite decreases significantly with decreasing temperature; at 1200°C (point C in Figure 1) the extent of substitution is 62 mol. % $MnTa_2O_6$.

The MnO content of natural tapiolites and the FeO content of natural tantalites, as shown in compilations of analyses (Palache, Berman and Frondel, 1944, pp. 776 and 783), are mostly within the limits shown in Figure 1. The comparison is not exact because of the presence of additional components, especially Nb_2O_5, in the natural materials. However, some of these samples include coexisting tapiolite and tantalite; in these cases, failure to achieve complete separation would tend to cause the analysis to plot in the two-phase region.

The analyses of ferroan tantalites (ibid p. 783) are of material that was not positively distinguished from tapiolite. Figure 1 suggests that the iron content of tantalites is so limited that "ferroan tantalites" cannot exist. The substitution of niobium for tantalum increases the limit of iron content, but experimental work by Schröcke (1965) suggests that the limit reaches 50 mol. % (Fe:Mn = 1) only at Nb:Ta = 1 (1100°C). Therefore, the essential end-member of the tantalite series is $MnTa_2O_6$, and the prefix "mangano" is redundant.

The effect of the Fe-Mn substitution on cell size can be seen in Table I.

THE SYSTEM $MnTa_2O_6$ - $FeTa_2O_6$ - O

The oxidation of tantalites and tapiolites in the system $MnTa_2O_6$-$FeTa_2O_6$ was studied at various partial pressures of oxygen, and the results are shown in Figures 2(a) and 2(b). The base of these diagrams is the 1200°C isotherm from Figure 1, and points marked A, B, C and D are at the boundaries of the fields of tantalite and tapiolite thereon.

End-member tantalite, $MnTa_2O_6$, remains stable under the most oxidizing condition, which was 1 atm. P_{O_2}. By contrast, the iron-bearing compounds are not stable and are oxidized according to the equation:

$$2\,Fe^{+2}Ta_2O_6 + \tfrac{1}{2}O_2 \rightleftharpoons 2\,Fe^{+3}TaO_4 + Ta_2O_5 \quad \ldots\ldots \text{(Eq 1)}$$

For end-member tapiolite, $FeTa_2O_6$, this oxidation reaction has already been described (Turnock, 1965). Ta_2O_5 was exsolved, but the $FeTaO_4$ remained in solid solution by the substitution:

$$Fe_2Ta_4O_{12} \longleftrightarrow Fe_3Ta_3O_{12} \quad \ldots\ldots\ldots\ldots \text{(Eq 2)}$$

These solid solutions, which are stable at relatively low oxygen pressures, were found to take up to 22 mol. % $Fe_3Ta_3O_{12}$ into solid solution according to Equation 2, at 1200°C. Solid solutions containing 30 to 100 mol. % $Fe_3Ta_3O_{12}$, which formed at higher oxygen pressures, had a rutile-type structure with an A_2O_4 unit cell.

The presence of manganese in solid solution affects the stability of tapiolites, making them more resistant to oxidation. This is illustrated in Figure 2(a) by the manner in which the oxygen pressure isobars radiate out from the $MnTa_2O_6$ corner. The oxidation of the iron in manganian tapiolites is also described by Equations 1 and 2, because the manganese

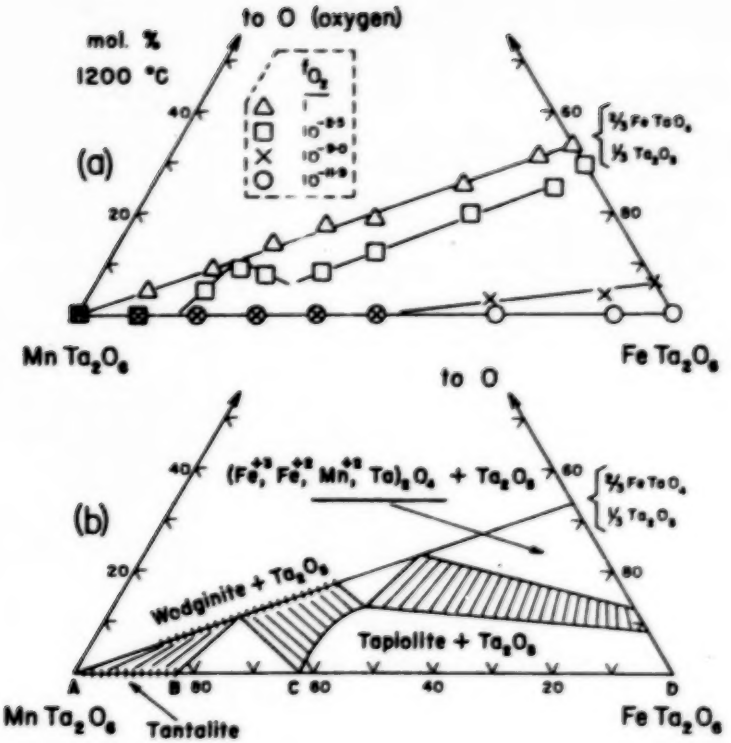

Figure 2. The join $MnTa_2O_6$-$FeTa_2O_6$-O at 1200°C, total pressure = 1 atm. (a) Plot of bulk compositions of solid phases at various oxygen pressures (f_{O_2}), giving isobaric tie-lines. (b) Stability fields of the solid phases. Hatched lines indicate solid solution along a line. Three-solid phase fields are ~~lines~~, four-solid phase fields are triangles.

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remains divalent. At intermediate oxygen partial pressures, the ferric iron produced by reaction (1) remains in solid solution by Equation 2, with small amounts of Ta_2O_5 being exsolved, so that tapiolite has a field of stability shown in projection in Figure 2(b).

At higher oxygen partial pressures (see Figure 2(a)), tapiolite is oxidized to form Ta_2O_5 plus either one or both of wodginite and a rutile-type compound (Figure 2(b)).

The tantalites, which are stable up to high oxygen pressures, also react by the oxidation of the iron-bearing component according to reaction (1). Tantalite, however, did not incorporate any ferric iron into solid solution. Instead, wodginite and Ta_2O_5 formed and the composition of the tantalite changed towards the $MnTa_2O_6$ end-member as this oxidation proceeded (Figure 2(a)).

The bulk compositions of the products of $(Mn^{+2}, Fe^{+2})Ta_2O_6$ materials that were heated in air or oxygen atmospheres plotted along the join $MnTa_2O_6 - \left[2/3\ FeTaO_4 + 1/3\ Ta_2O_5\right]$. The weight gain involved in this oxidation corresponds to the oxidation of the iron content, indicating that the wodginite and the rutile-type products on this join contained iron in the trivalent state and manganese in the divalent state.

It was known (Turnock, 1965) that the end-member of the rutile-type compound is $FeTaO_4$. The occurrence of exsolved Ta_2O_5 with wodginite and with the rutile-type compound suggested that both these compounds have compositions on the join $MnTa_2O_6$ - $FeTaO_4$.

THE SYSTEM $Mn_2Ta_4O_{12}$ - $Fe_3Ta_3O_{12}$

The formulae for the end-member molecules have been chosen so that the numbers of cations and oxygens would be equal. The results of syntheses in air (furnace atmosphere) of compositions on this join were: (i) Tantalite ($MnTa_2O_6$), which does not take ferric iron into solid solution; (ii) monoclinic wodginite $Mn^{+2}_{2-2w}Fe^{+3}_{3w}Ta_{4-w}O_{12}$ (w = mol. fraction of $Fe_3Ta_3O_{12}$), which has a range $0.08 < w < 0.29$ at 1200°C; and (iii) a rutile-type compound $Fe^{+3}_{3-3z}Mn^{+2}_{2z}Ta_{3+z}O_{12}$ (z = mol. fraction of $Mn_2Ta_4O_{12}$), which has a range $0 \leq z < 0.57$ at 1200°C.

These compositions are indicated on the left-hand side of the triangle in Figure 3.

Cell dimensions of these compounds are listed in Table I.

This synthetic wodginite is a compound of MnO, Fe_2O_3, and Ta_2O_5; therefore other elements found in natural wodginites, such as tin, appear not to be essential for its formation.

THE SYSTEM $Mn_2Ta_4O_{12}$ - $Fe_2Ta_4O_{12}$ - $Fe_3Ta_3O_{12}$

A preliminary isothermal diagram of this system is presented in Figure 3. The boundaries of the tapiolite field and of the field of the rutile-type ferri-tantalate are approximately known by projection from Figure 2(b). The contours of oxygen fugacity are projected from Figure 2(a).

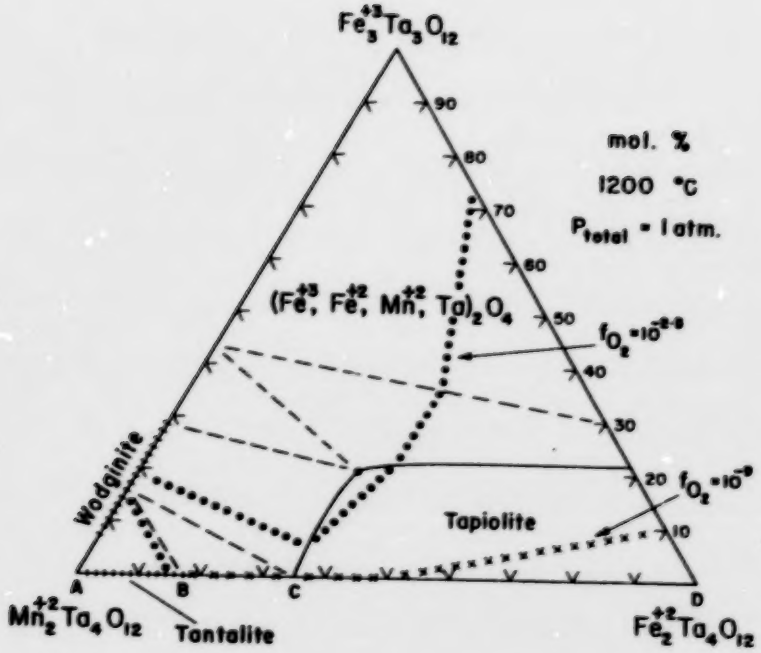

Figure 3. The system $Fe_3Ta_3O_{12}$-$Mn_2Ta_4O_{12}$-$Fe_2Ta_4O_{12}$ at 1200°C, total pressure = 1 atm. Field boundaries in the ternary are drawn by extrapolation from the sides, plus projection from the system $MnTa_2O_6$-$FeTa_2O_6$-O for the tapiolite field.

MINERALOGICAL CONSIDERATIONS

In nature, wodginite, tapiolite and tantalite are found in certain granitic pegmatites. Such pegmatites are greatly enriched in Ta, and some are also enriched in one or more of the elements Nb, Sn, Fe and Mn. Where this chemical enrichment has been achieved in a pegmatite magma, the partial pressure of oxygen will control which mineral or minerals will form and the Fe^{+3}/Fe^{+2} ratio therein, in a manner such as is illustrated in Figure 3.

Tapiolite is relatively the most common of the tantalates considered here; Palache et al. (1944, p. 777) mention about a dozen localities. In general, its presence indicates genetic conditions of relatively low oxygen pressures; specifically, the ratio Fe^{+3}/Fe^{+2} could be a univariant indicator of oxygen fugacity (univariant here meaning that the temperature must be determined independently, also that the effect of variable total pressure must be negligible).

The analyses of tantalites listed in Palache et al. (1944, p. 783) include only three (ibid, numbers 11, 12 and 14) which are low in iron. Those with high iron contents (ibid, numbers 13 and 15) are suspected, by comparison with Figure 1, of being tapiolites erroneously identified as ferrotantalites. As shown in Figures 2 and 3, tantalite is stable over a relatively large range of oxygen pressures. Its rarity is probably a reflection of the limits of the manganese content in pegmatites.

Wodginite is known from three localities (Nickel et al. 1963(a)). Its occurrence either without other tantalates, or with tantalite, indicates genetic conditions of relatively high oxygen pressure. In the Bernic Lake pegmatite, wodginite and tapiolite are in close association. This assemblage is at least bivariant; it could have been produced either in equilibrium with an intermediate partial pressure of oxygen, or by an incomplete oxidation reaction of manganian tapiolite to produce wodginite, or by the reverse reduction reaction.

The rutile-type ferri-tantalate, which has the largest range of Fe^{+3}/Fe^{+2} of all the compounds mentioned in Figure 3, is not known as a mineral, but its occurrence is predicted. It is possibly represented by ixiolite (Nickel, Rowland and McAdam, 1963(b)), which could have a polymorphic relationship to the rutile structure such as that described by Schröcke (1962) for the system $FeNbO_4$-$FeTaO_4$, and by Laves et al. (1963) and by Roth and Waring (1964) for $FeNbO_4$.

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REFERENCES

1. Broch E.K. (1929): Untersuchungen über Kristallstrukturen des Wolframittypus und des Scheelittypus, Skrifter Norske Vid.-Akad. Oslo, I, Mat.-Nat.Klasse, Bd.3, No.8.

2. Darken L.S. and Gurry R.W. (1945): The System Fe-O. I. The Wüstite Field and Related Equilibria, J. Am. Chem. Soc., 67, (II), 1398-1412.

3. Laves F., Bayer G. and Panagos A.(1963): Strukturelle Beziehungen zwischen den Typen der α-PbO_2, $FeWO_4$ (Wolframit) und $FeNb_2O_6$ (Columbit), und über die Polymorphie des $FeNbO_4$, Schweiz. Min. Petrogr. Mitt., 43, 217-34.

4. Nickel E.H., Rowland J.F. and McAdam R.C. (1963(a)): Wodginite-a new Tin-Manganese Tantalate from Wodgina, Australia, and Bernic Lake, Manitoba, Can. Min., 7. 390-402.

5. Nickel E.H., Rowland J.F. and McAdam R.C. (1963(b)): Ixiolite-a columbite substructure, Am. Min., 48, 961-79.

6. Palache C., Berman H. and Frondel C. (1944): Dana's System of Mineralogy, seventh ed., vol. I. Wiley and Sons, N.Y.

7. Roth R.S. and Waring J.L. (1964): Ixiolite and other polymorphic types of $FeNbO_4$, Am. Min., 49, 242-46.

8. Sasaki A. (1959): Variation of Unit Cell Parameters in Wolframite Series, Min. J. (Japan), 2, 375-96.

9. Schröcke H. (1961): Heterotype Mischbarkeit zwischen Wolframit-und Columbitgruppe, Beitr. Min. Petrog., 8, 92-110.

10. ——— (1962): Heterotype Mischbarkeit zwischen Wolframit-und Rutilgruppe, Beitr. Min. Petrog., 8, 339-48.

11. ——— (1965): Personal communication.

12. Turnock, A.C.(1965): Fe-Ta Oxides: Phase Relationships at 1200°C, J. Am. Ceramic. Soc., 48, 258-261.

TABLE I

Cell Dimensions of Synthetic Iron/Managanese Tantalates

Material	a (A)	b (A)	c (A)	β	V (A^3)
Tantalites:					
$MnTa_2O_6$	5.768	14.454	5.097		424.9
$Mn_{0.9}Fe_{0.1}Ta_2O_6$	5.763	14.436	5.094		423.8
$Mn_{0.85}Fe_{0.15}Ta_2O_6$	5.765	14.430	5.093		423.7
Tapiolites:					
$Fe_{0.4}Mn_{0.6}Ta_2O_6$	4.765		9.276		210.6
$Fe_{0.5}Mn_{0.5}Ta_2O_6$	4.762		9.264		210.1
$Fe_{0.7}Mn_{0.3}Ta_2O_6$	4.761		9.221		209.2
$Fe_{0.9}Mn_{0.1}Ta_2O_6$	4.758		9.207		208.3
$FeTa_2O_6$	4.756		9.198		208.0
Wodginites:					
$Mn_{1.8}Fe_{0.3}Ta_{3.9}O_{12}$	9.479	11.441	5.096	91°08'	552.5
$Mn_{1.6}Fe_{0.6}Ta_{3.8}O_{12}$	9.456	11.416	5.091	91°01'	549.5
Rutile-type compounds:					
$Fe_{1.5}Mn_{1.0}Ta_{3.5}O_{12}$	4.713		3.079		68.37
$Fe_{1.8}Mn_{0.8}Ta_{3.4}O_{12}$	4.704		3.069		67.89
$FeTaO_4$	4.678		3.047		66.74

Materials synthesized at 1200°C, 1 atm. total pressure. X-ray diffractometer measurements on powder made at room temperature, cobalt radiation K_{α_1} $\lambda = 1.7889$ A. Internal standard used was Si, with 2θ (220) = 55.532°. Errors are estimated to be $\pm$ 0.08% on cell edges.